

PATENT SPECIFICATION

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(54) PERFUME CARRIERS BASED ON CARBOXYMETHYL CELLULOSE GELS

(71) We, BAYER AKTIEN-GESELLSCHAFT, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to novel perfume carriers based on stable carboxymethyl cellulose gells containing water and, optionally, alcohols.

15 It is generally known that gels may be used as perfume carriers. Thus, U.S. Patent Specification No. 2,691,615 describes perfume carriers based on alginates, gelatin, pectin, agar-agar, karaya and tragacanth gums and starch. The gels are either reversible or irreversible. They are irreversible in cases where alginates are used as the gel formers and are crosslinked with divalent metal ions, especially calcium, barium, strontium and magnesium ions.

25 U.S. Patent Specification No. 2,972,055 describes as bases for perfume carriers, mixtures of carragenates and carob bean flour, to which carboxymethyl celluloses are added to improve the gel properties. Perfume carriers of this kind are produced by mixing perfumes with aqueous dispersions of the gel formers which may also contain other additives, heating the dispersion to temperatures of up to 86°C until a homogeneous solution is obtained and then reducing the temperature until gelation occurs. Gels of this kind are completely reversible because they become liquid again on heating and re-solidify on cooling.

45 Unfortunately, these conventional products are attended by serious disadvantages. In general, gels can only be reproducibly formed from naturally occurring substances when the starting

materials have a high degree of purity. This means that only high-quality products can be used which in general can only be obtained by technically complicated purification processes. In addition, the starting materials are often not available in sufficient quantities. 50

Another disadvantage of the natural substances is that their properties are only variable to a limited extent. Although gels of various classes of natural substances differ in their properties to a certain extent, it is difficult optimally to adapt their property spectrum to the properties required for the particular perfume because the perfumes can differ very widely with regard to their chemical structure. For example, they may have a terpene structure, but may also contain ester, ether or ketone functions. Accordingly, it would be desirable to have gel compositions whose structure could be optimally adapted to the perfume so as to ensure maximum and uniform release of the perfume over a period of time. 55 60 65 70

Apart from the alginate gels crosslinked by divalent metal ions, all other gel compositions do not have any dimensional stability under heat. Depending upon the chemical nature of the gel matrix and upon the composition of the gel, the gels begin to flow at temperatures as low as 40°C. In cases where such gels are used as perfume carriers, this behaviour naturally gives rise to problems where the outside temperatures are high, as for example in tropical and subtropical climates. In extreme cases, the perfume carrier coalesces into a flat, pasty mass. 75 80 85

It is also known that aqueous solutions of sodium carboxymethyl cellulose can be solidified by the addition of trivalent metal ions to form gel compositions whose stiffness may vary within certain limits. J. B. Batdorf and J. M. Rossman reported on materials of this kind in their work 90

"Industrial Gums, polysaccharides and their Derivatives", Academic Press, New York and London, 1973. Gels of this kind are irreversible because they do not undergo any change in their aggregate condition as a result of an increase in temperature.

It has now been found that gel-based temperature stable perfume carriers, whose properties can be varied within wide limits and which uniformly release their perfume content, can be obtained by using carboxymethyl cellulose as gel former and crosslinking it with at least trivalent metal ions.

This discovery must be very surprising to the expert because it is generally known that polymers containing carboxylate groups are crosslinked to a greater extent, the higher the valency of the crosslinking metal cation. In cases where trivalent metal ions are used, therefore, very densely crosslinked products, which might have been expected to release no further perfume from their "cage structure", are formed from sodium carboxymethyl cellulose. All the more surprising is the discovery that even very heavily crosslinked gel structures release the perfumes in the same way as non-crosslinked, highly viscous aqueous sodium carboxymethyl cellulose solutions.

The gels thus obtained have a number of advantages over conventional perfume carrier gels:

As a semi-synthetic product, sodium carboxymethyl cellulose is inexpensively available virtually throughout the world in a reproducible high quality in contrast to pure natural substances. By modifying their structure, in particular by varying the carboxyl group content, it is possible to produce gels whose properties may be optimally adapted to meet the requirements of the particular perfume used.

In contrast to the natural substances previously discussed satisfactory perfume carrier gels may even be produced with relatively impure qualities of sodium carboxymethyl cellulose. This makes the process used for producing the gels less critical, widens the range of raw materials from which they may be produced and reduces raw material costs because there is no need for expensive purification processes.

By comparison with various natural gel formers, there is the further advantage that gel formation, which takes place at the same time as the crosslinking reaction, is actually obtained at room temperature rather than at elevated temperatures. The undesirable premature evaporation of sensitive perfumes having a low boiling point is avoided in this way so that, in the

finished perfume carrier, there is no change of odour in relation to the perfume composition used.

The perfume carriers based on carboxymethyl cellulose according to the invention are less sensitive to micro-organisms than pure natural gels. 70

The temperature-stable perfume carriers having a readily variable property spectrum may be obtained by reacting sodium carboxymethyl cellulose dissolved in water with polyvalent metal ions in the presence of perfumes, optionally alcohols and optionally other additives. 75

The expression "gel" applied to perfume carriers of the kind in question is intended more to describe the physical condition of the jelly-like end product than to reproduce the exact polymer-physical structure in accordance with the temporary views of colloid chemists on this condition. 80 85

Reaction of the individual components to form the gels may be spread out from the point of view of time and takes place spontaneously or after several minutes or hours, depending upon the reactants and reaction conditions. Production of the perfume carriers may be readily carried out continuously, which is of considerable advantage for numerous applications. 90 95

Accordingly, the present invention relates to perfume carriers based on carboxymethyl cellulose gels and to a process for their production, which is distinguished by the fact that aqueous solutions of a carboxymethyl cellulose are reacted with solutions and/or dispersions of salts of at least trivalent metals in water and/or hydrophilic solvents in the presence of perfumes and, optionally, other additives. 100 105

Dispersants suitable for gel formation include both pure water and also mixtures of water and up to 40% by weight of alcohols so that the gels may even be regarded either as hydrogels or as alcohol gels. Suitable alcohols include both readily volatile monoalcohols, such as ethanol, isopropanol or butanol, and also substantially involatile polyalcohols, such as ethylene glycol, diethylene glycol or glycerol. Water is preferably used as the dispersant. 110 115

The perfume carriers may be produced in different ways. Thus, it is possible to combine all the components, i.e. the carboxymethyl cellulose, the dispersant, i.e. water and alcohol, the perfume carrier, the polyvalent metal compound and the other additives used, if any, at once. However, the components are preferably combined in stages. In this case, the perfume is dissolved or emulsified in an aqueous solution of carboxymethyl cellulose either on its own, or in admixture with other additives such as 120 125 130

dyes, preservatives or emulsifiers. At the same time, a solution or dispersion of the salt of a trivalent metal, used as crosslinking agent, in water or hydrophilic solvents such as alcohols, ketones, esters or ethers is prepared and the two solutions or dispersions subsequently mixed with one another, taking into account stoichiometric quantitative ratios.

The mixture is poured into moulds in which the reaction by which the perfume carrier gel is formed generally takes place over a period ranging from a few seconds to a few minutes.

Depending on various parameters, the end product is soft to very firm and may either be compact or foam-like. The end product is foam-like in cases where air is injected into or mixed with the gel-forming mixture before it hardens.

Production of the perfume carrier is made easier and the quality of the gels improved by intensively mixing the starting components. In the most simple case, mixing may be carried out in a zone of high turbulence generated by means of a mechanical stirrer. Better results are obtained by using high-speed mixers, for example impeller-type homogenising machines or stirrer-equipped mixing chambers of known and commercially available polyurethane foaming machines. However, intensive mixing may also be obtained by using mixers of polyurethane foaming machines in which the mixing effect is obtained by countercurrent injection.

So far as gel formation is concerned, the quantity of water and, optionally, alcohol present is not critical and may be varied within wide limits. The quantity of alcohol and water may amount to 98%, based on the total weight of the gel. However, the properties of the gels obtained are heavily influenced by the quantitative ratio between polymer and dispersant. In general, gels with decreasing polymer content are softer and structurally less firm. The quantity of carboxymethyl cellulose in the perfume carriers preferably amounts to 0.5 and 10% by weight, although the quantity to be used in any given case is determined to a large extent by the type of carboxymethyl cellulose used, i.e. by its molecular weight and degree of substitution.

The properties of the gels are also influenced to a considerable extent by the concentration of crosslinking metal ions. In general, the concentrations of the metal salts, based on the total weight of the gel, amount to between 0.2 and 5% by weight and preferably to between 0.5 and 3% by weight. In this case, too, the limits are again wide and are determined by the type of

metal salt used and also by the molecular weight and degree of substitution of the carboxymethyl cellulose used. For a given quantity of sodium carboxymethyl cellulose, the gels are generally harder and more rubber-like, the higher the concentration of metal salts. The quantity of metal ions (if one metal equivalent is associated with each carboxylate group) may be substantially equivalent or may even be present in a deficit, based on the number of carboxylate groups in the sodium carboxymethyl cellulose. Naturally the densest polymer networks are obtained where the equivalent procedure is adopted.

The quantity of perfumes used in the preparation of the perfume carrier gels is not a critical factor either and is determined by the particular duration of perfume release required. As expected, the perfume carriers remain release-active for longer periods, the more perfume they contain. In general, the perfume carriers contain the perfumes in quantities of from 1 to 20% by weight.

One particularly surprising aspect of the gel-based perfume carriers according to the invention is that they are extremely stable. Even after prolonged storage, there is no sign of phase separation which would be reflected for example in clouding of the material. By virtue of its irreversibility, the gel retains its dimensional stability without any phase separation, even when stored at elevated temperatures. The dispersant is very firmly anchored in the gel, which is the reason why the gels do not show any syneresis. Even after they had been stored for several weeks at 54°C, the perfume carrier gels according to the invention showed only negligible signs of syneresis.

Although the dispersant is anchored very firmly in the gel, it can egress more or less quickly, according to its vapour pressure, if the gel is left standing in the open, as a result of which the gel gradually shrinks proportionally to its external dimensions. During shrinkage the perfume also diffuses out from the gel base and evaporates into the atmosphere.

Starting materials for the perfume carriers according to the invention include any standard types of sodium carboxymethyl cellulose of commercial, cosmetic or food quality. In general, these polymers are characterised by the viscosities of their 2% aqueous solutions. The qualities suitable for production of the perfume carrier gels have viscosities of from 6 to 60,000, preferably from 20 to 30,000 centipoises, at a temperature of 20°C. Accordingly they have molecular weights of from 80,000 to 700,000, preferably from 100,000 to 500,000. The

degree of etherification of these products is generally between 0.25 and 1.4, in other words each glucose unit contains on average from 0.25 to 1.4 sodium carboxylate groups.

In the production of the perfume carrier gels, the salt content of the sodium carboxymethyl cellulose (mainly sodium chloride and sodium sulphate) is another critical factor. The salt content may readily amount to between 1 and 50% by weight, based on the dry carboxymethyl cellulose.

Other starting materials for the perfume carriers according to the invention are salts of at least trivalent metals which may be both soluble and also insoluble in the dispersant. It is possible to use both water-soluble and also water-insoluble salts. The solubility of the salts determines the crosslinking rate and hence the gel-forming rate. Water-soluble compounds lead to rapid gel formation. In many cases, it is often of particular advantage to use metal salts of relatively poor solubility, because they provide the gel-forming mixtures with a longer processing time. Accordingly, the processing time may be adjusted according to the particular metal salt or metal salt mixture used.

The following are typical examples of metal salts suitable for use in accordance with the invention: aluminium sulphate . 18 H₂O, basic aluminium acetate, iron (III) phosphate . H₂O, aluminium acetate, aluminium chloride . 6 H₂O, sodium-, potassium- and ammonium-aluminium alums, iron (III) chloride . H₂O, iron (III) nitrate . 9 H₂O, iron (III) sulphate, chromium (III) chloride . 6 H₂O, chromium (III) sulphate . 18 H₂O and aluminium sulphate chelates with citric acid, maleic acid, oxalic acid, malonic acid, lactic acid and malic acid.

Perfumes suitable for making up the perfume carriers in accordance with the invention are any of the fragrant individual components or compositions known under the names of etherial oils, scents or odoriferous substances. So far as the process according to the invention is concerned, it is immaterial whether the perfumes are soluble in the dispersant or whether they can only be emulsified or dispersed therein.

Etherial oils are, for example, anise oil, bergamot oil, camphor oil, citronella oil, lemon oil, eucalyptus oil, pine needle oils, geranium oil, lavender oil, lemon grass oil, clove oil, orange oil, orange peel oil, peppermint oil, rose oil, oil of spike, terpentine oil and oil of cinnamon.

They are complicated mixtures of alcohols, aldehydes, ketones, esters, oxides,

lactones, terpenes and many other, in some cases still unresolved compounds.

In the context of the invention, odoriferous substances are chemically precisely defined individual compounds which may either be isolated from etherial oils or synthetically produced, such as for example anethol, anisaldehyde, vanillin or citronellal. Scents are perfume mixtures in a solvent, the perfume mixtures again consisting of etherial oils and odoriferous substances.

In the production of the perfume carriers, it is also possible to add a considerable quantity (up to about 50% by volume) of a variety of different fillers such as silicates, various types of silica, aluminium oxides, tin oxides, antimony trioxide, titanium dioxide, graphite and graphitised carbon, carbon black, retort carbon, blown sand, powdered cements, a variety of different inorganic and organic pigments, for example iron oxide pigments, lead chromate, lead oxide and red lead. Other suitable fillers are long and short fibers of natural or synthetic materials, such as for example cellulose powder. One advantage of using fillers is that they lengthen the perfume-release period of the gel base.

It is also possible, during production of the perfume carriers, to add preservatives which prevent the growth of bacteria and molds, or even surfactants or solutions of other natural or synthetic polymers. It is also possible to add water-soluble dyes, perfume carriers such as isopropyl alcohol, or substances for increasing water-retention capacity, such as ethylene glycol, polyethylene oxides, glycerol, sorbitol, starch, urea, triethanolamine or polyvinyl alcohol, during production of the perfume carriers.

In addition, a gaseous component may be added during gel formation. It is possible in this way to form foam-like perfume carriers whose unit weight (kg/m³) is more or less greatly reduced in relation to the compact material, depending upon the quantity of gas incorporated. One particular advantage of the process according to the invention is that it is very easy to carry out continuously.

To this end, the sodium carboxymethyl cellulose dissolved in the dispersant, in which the perfume and the other additives used, if any, are also dissolved or dispersed, and the solution or dispersion of the metal salt are continuously introduced separately therefrom at room temperature or at a higher temperature (up to about 40°C) into a mixing zone in such a quantity that crosslinking is not actually completed in that zone. The still fluent and deformable carboxymethyl cellulose gel with its high

water and alcohol content is then continuously removed from the mixing zone and optionally passed through a short dwell pipe which is provided with a profiled end piece so that the carboxymethyl cellulose gel formed is obtained in the form of a shaped, endless strand, ribbon or sheet.

The perfume carriers obtained may be used for a variety of different applications where freshening of air is required, including both the domestic sector and also the industrial sector.

EXAMPLE 1

a) Preparation of the carboxymethyl cellulose solution

50 parts by weight of carboxymethyl cellulose (CMC) are gradually added with intensive stirring at room temperature to 950 parts by weight of water. The CMC used is a normally etherified CMC, a 2% solution in water of which has a viscosity at 20°C of 25 to 32 centipoises. Stirring is continued until a clear, lump-free solution has formed. Depending upon the type of CMC used, the dissolution process may be facilitated by initially moistening the CMC with a water-miscible liquid, for example alcohol or glycerol, and then stirring it into the water.

b) Preparation of the gel

7 parts by weight of perfume oil (mixture of 80% by weight of isobornyl acetate and 20% by weight of the condensation product of 1 mole of nonyl phenol and 10 moles of ethylene oxide) and 10 parts by weight of isopropanol are simultaneously or successively added to 100 parts by weight of the CMC-solution described above, followed by intensive mixing for 60 seconds. 20 parts by weight of a 9% by weight aqueous AlCl_3 -solution are then added while stirring, after which the mixture hardens in 1 second to form a hard, rubber-like gel.

EXAMPLE 2

The gel is prepared in the same way as in Example 1. Instead of 9% aluminium chloride solution, 20 parts by weight of a 4.5% aqueous AlCl_3 -solution are used. In this case, a soft, stable gel is formed in 1 second.

EXAMPLE 3

The procedure is the same as in Example 1. Instead of the aqueous aluminium chloride solution, 20 parts by weight of a 9% dispersion of $\text{Al}(\text{CH}_3\text{COO})_2\text{OH}$ in water are added. The mixture is intensively stirred for 30 seconds. This mixture remains pourable for approximately 30 minutes, only reaching a viscosity of 20,000 centipoises after 30 minutes. Thereafter it

continues gradually to harden into a rubber-like hard gel.

EXAMPLE 4

The procedure is as in Example 3. Instead of the 9% dispersion, 20 parts by weight of a 4% dispersion of $\text{Al}(\text{CH}_3\text{COO})_2\text{OH}$ in water are added, followed by stirring for 30 seconds. The mixture formed remains pourable for up to 60 minutes. It then continues gradually to harden into a soft, stable gel.

If, after shaping, this gel is stored for 1 week in a suitable, sealed plastics container at a temperature of 54°C, it retains its original shape. The weight loss through discharged and condensed liquid amounts to 1.52% of the original weight of the shaped gel before storage. The fragrance note produced by the processed perfume oil is unaffected by the period of storage.

EXAMPLE 5

The procedure is the same as in Example 4, except that the 4.5% $\text{Al}(\text{CH}_3\text{COO})_2\text{OH}$ -dispersion additionally contains 0.035% of AlCl_3 in dissolved form. The mixture formed after stirring remains pourable for 25 minutes. Thereafter it continues to harden into a soft, stable gel.

EXAMPLE 6

The procedure is as in Example 5, except that the 4.5% $\text{Al}(\text{CH}_3\text{COO})_2\text{OH}$ -dispersion additionally contains 0.7% of AlCl_3 in dissolved form. The mixture formed after stirring remains pourable for 5 minutes. Thereafter it continues to harden into a soft, stable gel.

EXAMPLE 7

The procedure is the same as in Example 4. If 20 parts by weight of a 3.5% aqueous $\text{Al}(\text{CH}_3\text{COO})_2\text{OH}$ -dispersion are used instead of the 4.5% $\text{Al}(\text{CH}_3\text{COO})_2\text{OH}$ -dispersion in water, a soft stable gel is formed. If, after shaping, this gel is stored for 1 week in a sealed, suitable plastics container at a temperature of 54°C, it retains its original shape. The weight loss through discharged and condensed liquid amounts to 14% of the original weight of the shaped gel before storage. The perfume note produced by the processed perfume oil is unaffected by the period of storage.

WHAT WE CLAIM IS:—

1. A gel-based perfume carrier comprising a perfume and, as a base, a carboxymethyl cellulose gel which contains water and is crosslinked by at least one at least trivalent metal ion.

2. A gel-based perfume carrier as claimed in Claim 1 in which the cellulose gel also contains an alcohol.

3. A gel-based perfume carrier as claimed in Claim 1 or Claim 2 in which the carboxymethyl cellulose gel is a sodium carboxymethyl cellulose gel.
- 5 4. A gel-based perfume carrier as claimed in any of Claims 1 to 3 containing from 0.5 to 10% by weight, of carboxymethyl cellulose.
- 10 5. A gel-based perfume carrier as claimed in any of Claims 1 to 4 containing from 0.2 to 5% by weight, of metal salts.
- 15 6. A gel-based perfume carrier as claimed in any of Claims 1 to 5 containing from 1 to 20% by weight, of perfume.
- 15 7. A gel-based perfume carrier as claimed in Claim 1 substantially as herein described.
- 20 8. A gel-based perfume carrier as claimed in Claim 1 substantially as herein described with reference to any one of the Examples.
- 25 9. A process for production of a gel-based perfume carrier as claimed in Claim 1 which comprises reacting an aqueous solution of a carboxymethyl cellulose with a solution and/or a dispersion of an at least trivalent metal salt in water and/or a hydrophilic solvent in the presence of a perfume.
10. A process as claimed in Claim 9 in which the aqueous solution also contains an alcohol. 30
11. A process as claimed in Claim 9 or Claim 10 in which the carboxymethyl cellulose is a sodium carboxymethyl cellulose.
12. A process as claimed in any of Claims 9 to 11 which is carried out in the presence of a filler and/or a preservative and/or a surfactant and/or a dye. 35
13. A process as claimed in Claim 9 substantially as herein described. 40
14. A process as claimed in Claim 9 substantially as herein described with reference to any one of the examples.
15. A gel-based perfume carrier when produced by a process as claimed in any of Claims 9 to 14. 45

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